

PATENT SPECIFICATION

NO DRAWINGS

1.044.771



Inventor: ROBERT GEORGE COCKERHAM

Date of filing Complete Specification: March 24, 1964.

Application Date: April 2, 1963.

No. 13070/63.

Complete Specification Published: Oct. 5, 1966.

© Crown Copyright 1966.

Index at acceptance:—C5 E(12C, B1A, B1N)

Int. Cl.:—C 07 c 7/00, C 10 g 23/00

COMPLETE SPECIFICATION

Improvements in or relating to the Purification of Hydrocarbons

We, THE GAS COUNCIL, a British Body Corporate of 1 Grosvenor Place, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the purification of hydrocarbons, which may be olefin-containing hydrocarbon mixtures.

It is common practice to purify hydrocarbon mixtures by treating them chemically with hydrogen over a catalyst, when sulphur compounds are converted to hydrogen sulphide, which may be separated by physical or chemical means in contrast to the organic compounds which contain sulphur, which cannot be so easily separated. The conditions of hydrogenation usually involve the use of an elevated temperature in the region of 300—400°C, and the hydrogen treatment is often applied successfully under pressure which materially assists the rate of chemical reaction. Such a desulphurisation process, applied to a low-gravity light distillate is described in our co-pending application No. 32113/62 (Serial No. 1,028,245) but the process can be applied to a wide range of similar hydrocarbon mixtures. These could include, for example, distillates which comprise mainly propane or butane, commonly known as "liquefied petroleum gases" (l.p.g.) as well as higher boiling distillates in the petrol and kerosene ranges.

According to the invention there is provided a method of removing sulphur compounds from a hydrocarbon feedstock by hydrogenating sulphur-containing compounds present in the feedstock with a hydrogenating gas over a hydrodesulphurisation catalyst, which hydrocarbon feedstock and/or hydrogenating gas contains olefins and/or carbon oxides, which

method comprises passing a mixture of the hydrocarbons in vapour form with the hydrogenating gas over the hydrodesulphurisation catalyst to convert the sulphur present into hydrogen sulphide, dividing the thus-treated mixture into a recycle stream and a product stream, removing hydrogen sulphide either from the thus-treated mixture before division into two streams, or from the product stream and optionally also from the recycle stream and using the recycle stream to dilute further untreated mixture before passing the diluted untreated mixture over the hydrodesulphurisation catalyst, wherein the proportion of the treated mixture which is recycled is sufficient to maintain the reaction temperature in the region of the hydrodesulphurisation catalyst at not more than 450°C. The proportion of the treated mixture to be recycled may be withdrawn either before or after the removal of the hydrogen sulphide. It is an advantage of the invention that in the recovery of treated mixture free from hydrogen sulphide by passing the gases and vapours leaving the hydrodesulphurisation stage through a bed of absorbing material whereby the hydrogen sulphide is absorbed, the recycling prevents the temperature of the absorption stage exceeding 450°C.

The invention is of particular application to light petroleum gases and light distillates which contain appreciable quantities of olefinic hydrocarbons. Commercially available light petroleum gases may contain 10% by volume or more of olefins; though most commercially available distillates at present contain not more than 0.5% by volume of olefinic hydrocarbons recent specifications have indicated that future distillates may contain substantial proportions.

The chemical reactions which are theoretically possible in the hydrodesulphurisation treatment of hydrocarbons over a catalyst include the following:—

1	Organic Sulphur Compound + Hydrogen	→ Hydrogen Sulphide + Hydrocarbon
2	Paraffin Hydrocarbon + Hydrogen	→ A paraffin with a lower carbon number + Methane
3	Paraffin Hydrocarbon + Hydrogen	→ Two paraffin hydrocarbons of lower carbon number
4	Aromatic Hydrocarbon + Hydrogen	→ Cycloparaffin
5	Olefin + Hydrogen	→ Paraffin

Over the catalysts used for reaction 1, reaction 5 proceeds simultaneously, but reactions 2, 3 and 4 are substantially avoided. In considering therefore the full-scale development of a desulphurisation process, it is necessary to bear in mind that reactions 1 and 5 are both exothermic.

Table I shows the quantity of heat liberated per gram molecule at the standard conditions

of temperature (25°C) and pressure (1 atmosphere absolute), by the hydrogenation of a number of olefins, all of which could be present in liquefied petroleum gases or low gravity distillates. It will be seen that the heat of hydrogenation is reasonably constant, a feature which corresponds to the hydrogenation of one double valency bond in an olefinic hydrocarbon.

15

TABLE I

Heats of Hydrogenation of various olefins

All expressed per gram/molecule in the gas phase at 25° C. and 1 atmosphere.

Olefin	Hydrocarbon produced by hydrogenation	Heat liberated (calories)
Propylene	Propane	29,700
n-Butene	n-Butane	30,120
Iso-Butene	Iso-Butane	28,110
n-Pentene	n-Pentane	30,000
Iso-Pentene	Iso-Pentane	28,240
3-Methyl-1 Butene	Iso-Pentane	30,000
2 Methyl-2 Butene	Iso-Pentane	26,750
Cyclopentene	Cyclopentane	26,330

For all practical purposes, the heat of hydrogenation of the sulphur compounds may be neglected, since the quantity of these compounds present in any distillate is unlikely to be greater than 1% (w/w).

The invention is also of particular application when the hydrogenating gas contains appreciable amounts of carbon oxides, as hydrogen also reacts exothermically with them. It may be that neither the olefins in the hydrocarbon feedstock alone, nor the carbon oxides

in the hydrogenating gas alone, are sufficient to raise the catalyst to an undesirable temperature, but that the temperature effects which are possible when both are present together may be such as to make recirculation desirable.

It is to be understood that it is necessary to provide sufficient hydrogen to react with all the olefins and carbon oxides present, and it is preferable to provide an excess of hydrogenating gas. A volumetric ratio of hy-

35

40

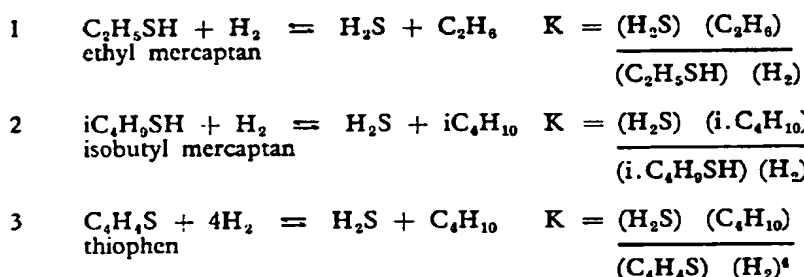
drocarbon vapour to hydrogen of between 3 or 4 and 10 to 1 may be appropriate.

The proportion of recycled gas to untreated mixture entering the hydrodesulphurisation catalyst is such as to maintain the temperature of that catalyst at not more than 450°C. The proportion of recycled gas necessary to maintain the catalyst at any desired temperature can be readily determined.

It is preferred that the hydrodesulphurisation is carried out at a temperature of from 250°C to 450°C, for example from 300°C to 400°C, and at a pressure of from 5 to 50 atmospheres or more, 25 atmospheres being a preferred pressure. The temperature limita-

tions are fairly critical in that below 250°C hydrocarbon vapours are liable to condense and above 450°C the catalyst activity is liable to fall off rapidly.

The hydrodesulphurisation catalyst may be molybdenum supported on alumina and promoted by cobalt or nickel, or any other suitable catalyst. However the performance of any catalyst is adversely effected as the temperature rises by the fact that the equilibrium constants then change in such a direction that a higher proportion of the organic sulphur compounds survive when equilibrium is attained. For example, in the reactions for three typical organic sulphur compounds:



the following data apply:

Compound	Value of K at		Ratio of proportion of organic sulphur surviving at 500° C. to that at 350° C. at equilibrium*
	350° C.	500° C.	
Ethyl mercaptan	4.37×10^5	3.47×10^4	12.6
Isobutyl mercaptan	1.38×10^5	2.24×10^4	6.2
Thiophen	2.09×10^6	63	3.3×10^4

* These ratios have been calculated by equating them with the ratios of the equilibrium constants.

Furthermore, when the vapours of hydrocarbons are heated to temperatures above 450°C under pressure in the presence of a conversion catalyst, with the small proportion of hydrogen required by the reactions, for example, a molybdenum catalyst supported on alumina and promoted by either nickel or cobalt, there is a tendency, variable in degree from catalyst to catalyst, for thermal decomposition of the hydrocarbons to occur leading to carbon deposition and a loss in activity of the catalyst. It is therefore desirable on both counts to limit the temperature of the conversion catalyst, in particular, to prevent it rising above 450°C. The loss of performance occasioned by the change in equilibrium constant on a rise of temperature is restored when the temperature is lowered; that resulting from

carbon deposition necessitates the removal of the deposit by controlled oxidation.

The hydrogen sulphide may be removed by bringing the treated mixture into contact with an absorbent capable of absorbing hydrogen sulphide, for example, the active iron oxide sold under the Trade Name "Luxmasse". It is known that the capacity for absorption of hydrogen sulphide by such iron oxide preparations declines if the temperature is raised substantially above 350°C, e.g. above 450°C and indeed that it is preferred to operate at as low a temperature as possible consistently with avoiding the condensation of the hydrocarbon vapour. If, therefore, vapours were to leave the conversion stage at a temperature substantially above 350°C, e.g., above 450°C, it would be advantageous to cool them before

they entered the absorption stage. The process of this invention provides an effective means of preventing gases and vapours entering the hydrogen sulphide absorption stage at an undesirable high temperature, without using cumbersome and inconvenient devices such as interstage cooling.

There is a pressure drop between the inlet and outlet of the hydrodesulphurisation catalyst, and a further drop across the absorption stage. It is necessary to raise the pressure of the recirculated gases and vapours sufficiently to allow them to enter and mix with the stream of fresh gases and vapours arriving at the inlet of the hydrodesulphurisation stage, by using a blower or other suitable means. The object of the invention, namely, to prevent the establishment of undesirably high temperatures by providing a sufficient mass of gases and vapours to absorb the heat of reaction is achieved whether the stream of gases and vapours to be recycled is withdrawn after the hydrodesulphurisation stage or after the hydrogen sulphide absorption stage. It is preferable, however, to withdraw the stream after the absorption stage, to avoid hydrogen sulphide, which is corrosive, entering the recirculating machine and the pipework on the recycle loop. This has the further advantage of ensuring that the mixture of fresh and recycled materials entering the hydrodesulphurisation stage contains no hydrogen sulphide, the presence of which would tend, in virtue of the equilibria on page 3, to lower the degree of purification obtained.

The invention is illustrated by the following comparative example.

EXAMPLE I

Commercial butane containing 20 per cent by weight of n-butene and 20 p.p.m. of organic sulphur when evaporated and mixed with 2 scf. of hydrogen per lb. of the hydrocarbon mixture is preheated to 380°C and passed over a nickel-promoted molybdenum catalyst supported on alumina in an insulated vessel so that there is no heat loss. The outlet temperature is 465°C. Heat loss from the reaction vessel would lead to a lower temperature being obtained, but one which might nevertheless seriously affect the results of hydrodesulphurisation. The product butane contains less than 0.2 per cent by weight of butene and less than 0.2 p.p.m. of sulphur (after absorption of the hydrogen sulphide).

When provision is made for recycling the product mixture of butane and residual hydrogen, after removal of the hydrogen sulphide, three volumes are recirculated per volume of the ingoing mixture, with the mixture entering the conversion catalyst being preheated to 380°C as before and the outlet temperature is 400°C. The product butane after removal of hydrogen sulphide contains no more butene and organic sulphur than when recirculation is not practised.

Some other form of cooling could be used, either of the vessel containing the catalyst externally, or by having within it, for example, coils of tubing through which a cooling medium could be circulated. This method may be impractical and unnecessarily complicated when compared to the method of the invention. The treated mixture will not evolve heat a second time, if passed over the catalyst, but will dilute the ingoing fresh reactants. The heat evolved from the latter will then raise the temperature of the mixture to a level which is less than it would be if fresh reagents only were being supplied to the catalyst by a factor which is proportional to the quantity of recycled materials.

WHAT WE CLAIM IS:—

1. A method of removing sulphur compounds from a hydrocarbon feedstock by hydrogenating sulphur-containing compounds present in the feedstock with a hydrogenating gas over a hydrodesulphurisation catalyst, which hydrocarbon feedstock and/or hydrogenating gas contains olefins and/or carbon oxides, which method comprises passing a mixture of the hydrocarbons in vapour form with the hydrogenating gas over the hydrodesulphurisation catalyst to convert the sulphur present into hydrogen sulphide, dividing the thus-treated mixture into a recycle stream and a product stream, removing hydrogen sulphide either from the thus-treated mixture before division into two streams, or from the product stream and optionally also from the recycle stream, and using the recycle stream to dilute further untreated mixture before passing the diluted untreated mixture over the hydrodesulphurisation catalyst, wherein the proportion of the treated mixture which is recycled is sufficient to maintain the reaction temperature in the region of the hydrodesulphurisation catalyst at not more than 450°C.

2. A method as claimed in claim 1 wherein the hydrocarbon feedstock contains olefins and sufficient hydrogen is provided in the untreated mixture to hydrogenate all the olefins present as well as the sulphur-containing compounds.

3. A method as claimed in claim 1 or claim 2 wherein the hydrogenating gas contains oxides of carbon, and sufficient hydrogen is provided in the untreated mixture to react with all the oxides of carbon as well as the sulphur.

4. A method as claimed in any one of the preceding claims wherein the hydrodesulphurisation catalyst is maintained at a temperature of from 300°C to 400°C.

5. A method as claimed in any one of the preceding claims wherein the hydrodesulphurisation is carried out at a pressure of from 5 to 50 atmospheres.

6. A method as claimed in any one of the preceding claims wherein separation of hydrogen sulphide from the treated mixture is effective.

ted before the recycle proportion is separated from the product.

- 5 7. A method of removing sulphur compounds from a hydrocarbon mixture as claimed in claim 1 and substantially as hereinbefore described in the Examples.

8. Hydrocarbons when purified by the

method claimed in any one of the preceding claims.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press
(Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings,
London, W.C.2, from which copies may be obtained.